September 3-10 2023

ISSPIC XXI

Berlin 2023

International Symposium on Small Particles and Inorganic Clusters XXI
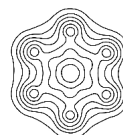
Graduate Student Seminar

ISSPIC XXI Berlin 2023

International Symposium on Small Particles and Inorganic Clusters

Graduate Student Seminar

September 02 –03, 2023 in Berlin/Germany

08:45   Welcome

Catalysis I

9:00   **Deepak Pradeep**
         3d metal doping of cobalt clusters to tune the activity toward CO_2

09:15   **Philip A. J. Pearcy**
         Infrared Photodissociation Studies of Nitric Oxide on Metal and Metal Oxide Centres

09:30   **Pavol Mikolaj**
         Activation of CO_2 by free metal oxide clusters

09:45   **Barbara Zamora**
         CO_2 and H_2 activation on zinc-doped copper clusters

10:00   **Arravind Subramanian**
         Chemical ordering of Au-Ni nanoparticles and their activities in oxygen reduction reaction

10:15   **Imran Abbas**
         Gas-phase Pd and PdZn clusters deposited on ZnO and SiO_2 as model catalyst for CO_2 hydrogenation to methanol

10:30   Coffee Break

11:00   **Christian Weigelt**
         Ultrafast wettability alteration: The decisive moments of adsorption on supported particles

Instrumental Developments

11:15   **João Coroa**
         Influence of the magnetic field configuration of a magnetron on the cluster growth mechanism in a sputtering gas aggregation source

11:30   **Maximilian Winzely**
         A novel electrochemical cell for the in situ X-ray absorption spectroscopic investigation of cluster-based CO_2-electroreduction catalysts

11:45   **Sumant Phadke**
         High-Pressure Grazing Incidence Cell for In Situ XAS Characterization of Nanoparticles on Planar Substrates under CO_2 Hydrogenation Conditions

12:00   **Bruno Ramirez-Galindo**
         Prospects and experimental challenges for matter-wave interferometry with massive metal clusters

12:15   **Lunch Break**

Ligated Clusters

13:45   **Saniya Gratious**
Surface Modulation on $Au_{25}(SR)_{18}$ NCs via the Ligand Exchange Induced Size/Structure Transformation

14:00   **Ye Liu**
Correlating the Impact of Heteroatoms Core-Tailoring of Atomically Precise $Ag_{25}(SR)_{18}$ Nanoclusters on the Photocatalytic Activities

14:15   **Shun Ito**
Evaluation of Superatomic Electronic Structures of Ligand-Protected Gold/Silver Superatoms by Gas-Phase Photoelectron Spectroscopy

14:30   **Ryosuke Ito**
π-π Interactions in Host-Guest Complexes Revealed by Cryogenic Ion Mobility-Mass Spectrometry

Structural, Electronic, and Magnetic Properties

14:45   **Yuto Nakajima**
Size dependent structures of platinum oxide cluster cations and anions studied by ion mobility-mass spectrometry

15:00   **Jie Zhao**
Effect of nanoparticle size on Boron-Doped Transition Metals

15:15   **Coffee break**

15:45   **Frederic Ussling**
X-ray induced explosion dynamics of methane clusters

16:00   **Tomoya Inoue**
Chemical Reactivity of Boron Substituted Aluminum Superatoms on Organic Substrates

16:15   **Dashjargal Arildii**
Characterization of Pyrrole Dimer Cations and Their Solvated Clusters by IR Spectroscopy

16:30   **Olesya S. Ablyasova**
Electronic state of a bis(μ-oxo) di-manganese oxide cluster revealed by XAS and XMCD

16:45   **Dominique P. Borgeaud dit Avocat**
Magnetic deflection of sodium doped solvent clusters

17:00   **Filip Rivic**
Magnetism of single-doped paramagnetic tetrel clusters studied by Stern-Gerlach experiments: Impact of the diamagnetic ligand field and paramagnetic dopant

Astro- and Atmospheric Chemistry

09:00 **Jessica C. Hartmann**
Searching for the Origin of Magic Numbers Amongst Sodium Chloride Clusters

09:15 **Sarah Madener**
Photochemistry of Pyruvate Embedded in Sea Salt Clusters

09:30 **Magdalena Salzburger**
Blackbody infrared radiative dissociation and master equation modelling of hydrated peroxycarbonate radical anions

09:45 **Tatsuya Chiba**
Observation of Penning Electron Detachment by Electronically-Excited Potassium Atoms in High Rydberg States

10:00 **Taarna Studemund**
Small Silicon Oxide Clusters – Optical Photodissociation and Photochemical Properties

10:15 **Nima-Noah Nahvi**
A modified particle in a box model

10:30 **Sascha Schaller**
Ionization and Dissociation Energies of Dysprosium Monoxide, DyO

10:45 **Coffee Break**

Catalysis II

11:15 **Dimitra Papamichail**
Gas-Phase CuPd Bimetallic Cluster-Modified Electrodes as Model Electrocatalysts for CO_2 Conversion

11:30 **Deema Balalta**
In situ (S)TEM Characterization of a Pd/ZnO Catalyst for CO_2 Hydrogenation and Selective Methanol Synthesis

11:45 **Filippo Romeggio**
Stable mass-selected AuTi nanoparticles for CO oxidation

12:00 **Esperanza Sedano Varo**
Size-studies of Au and Cu nanoparticles for CO_2 electroreduction: every parameter counts

12:15 **Nicola Da Roit**
Size dependence of catalytic activity of well-defined Pt nanosystem supported on CeO_2 for CO oxidation reaction

12:30 **Wenjian Hu**
Structure-selectivity of $Cu_{2-x}Se$ towards CO_2 electroreduction

12:45 **Hottopic Talk Voting**

Abstracts

3d metal doping of cobalt clusters to tune the activity toward CO_2

Deepak Pradeep,[1] Barbara Zamora Yusti,[2,3] Rutger Zijlstra,[1] Mate Szalay,[2,3] Tibor Höltzl,[2,3] László Nyulászi,[3] Joost M. Bakker[1]

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[2]Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, Hungary
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The increasing atmospheric CO_2 concentration leads to global warming and climate destabilization. One potential way to mitigate CO_2 emissions is by converting CO_2 into useful chemicals. In industry, for example, methanol is produced by direct hydrogenation of CO_2 over a $Cu-ZnO-Al_2O_3$ catalyst.[1] A detailed understanding of the reaction mechanisms is required for a rational design of more active and selective catalysts.

Gas-phase metal clusters can form an idealized model system for the active sites of the complex catalysts.[2] We aim to investigate on a molecular level how the doping of clusters with foreign elements affects their reactivity.[3] *To test this experimentally*, we aim to study the interaction of first-row transition metal-doped clusters with CO_2 and H_2 using IR photo fragmentation spectroscopy complemented by DFT calculations. For this, we present a newly commissioned dual-laser, dual-target cluster source and show how the doping of cationic cobalt clusters by single vanadium or iron atoms affects the adsorption mode of CO_2.
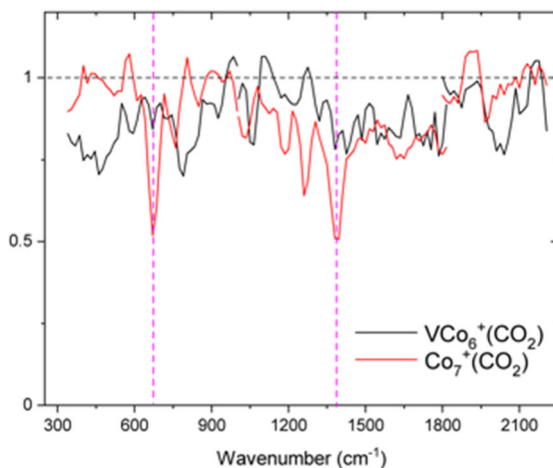

Figure 1: IR depletion spectra for cationic V-doped Co cluster and pure Co cluster with CO_2. The band near 2100 cm^{-1} (C-O stretch vibration) for the doped cluster indicates dissociation of CO_2.

[1] Waugh, K. C. Methanol Synthesis. Catal. Today, **15 (1)** (1992), 51–75.
[2] Lang, S. M.; Bernhardt, T. M. Phys. Chem. Chem. Phys., **14** (2012), 9255–9269.
[3] Szalay, M.; Buzsáki, D.; Barabás, J.; Faragó, E.; Janssens, E.; Nyulászi, L.; Höltzl, T. Phys. Chem. Chem. Phys., **23 (38)** (2021), 21738–21747.

Infrared Photodissociation Studies of Nitric Oxide on Metal and Metal Oxide Centres

Philip A. J. Pearcy[1], Gabriele Meizyte[1], Edward I. Brewer[1], Alice E. Green[1], Matthew Doll[1], Olga Duda[1], Peter D. Watson[1], Stuart R. Mackenzie[1].

[1] Department of Chemistry, University of Oxford, United Kingdom.

Nitrogen oxides, commonly known as NOx, are known to cause detrimental effects on the environment as well as on air quality [1]. This in turn can have a harmful effect on human health. Current mitigation strategies to deal with NOx includes using catalytic converters that harness the surface catalytic chemistry of transition metal atoms and clusters dispersed across a support [2]. Understanding the fundamental metal–ligand interactions that are important in catalytic chemistry between transition metal centres and nitric oxide (NO) molecules is therefore very useful. The isolated metal-ligand complexes can be studied using gas-phase infrared photodissociation (IRPD) spectroscopy in conjunction with quantum calculations. In my presentation, I will discuss our recent experimental and computational findings on the formation of NO dimers within Group 9 metal nitrosyl complexes ($M(NO)_n^+$, M=Co,Rh,Ir) [3], as well as our preliminary work on the differences between Pt and PtO nitrosyl clusters ($Pt/PtO(NO)_n^+$).
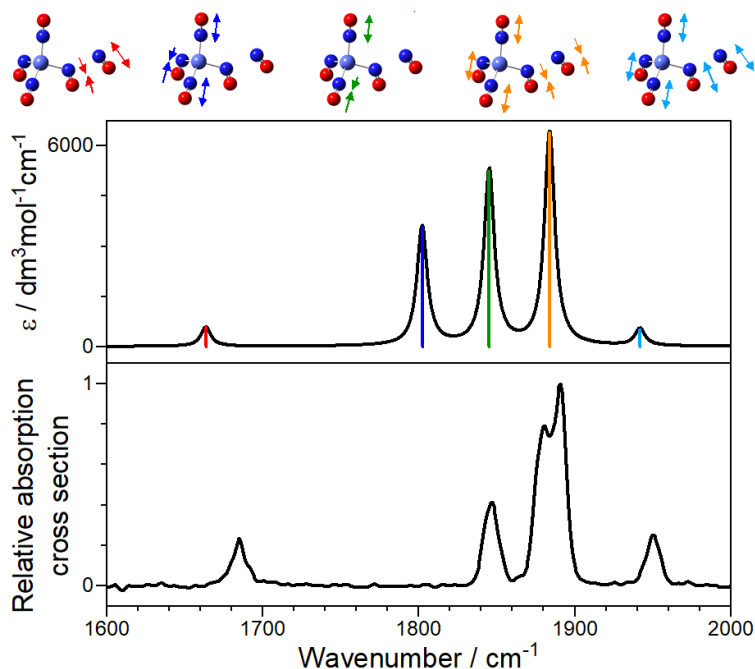

Figure 1: Top: Simulated spectrum of $Co(NO)_5^+$, with colour-coded mode vectors relating to the vibrations shown on the simulated species. Bottom: Experimental $Co(NO)_5^+$ IRPD spectrum.

[1]   T. Boningari, P. G. Smirniotis, Current Opinion in Chemical Engineering **13** (2016) 133–141
[2]   M. Shelef, Catalysis Reviews **11** (1975) 1-40
[3]   G. Meizyte, *et al.*, Journal of Physical Chemistry A **126** (2022) 9414-9422

Activation of CO_2 by free metal oxide clusters

Pavol Mikolaj, Sandra M. Lang, Thorsten M. Bernhardt

Institute of Surface Chemistry and Catalysis, Ulm University, Ulm, Germany

Motivated by the performance of the industrially employed Cu/ZnO catalyst for direct CO_2 hydrogenation [1], the European training network CATCHY [2] seeks to develop new and high-performance cluster-based catalysts. As part of this project, we utilize transition metal oxide clusters in the gas phase as model systems to study the fundamental driving forces that determine the reactive and catalytic properties of such catalysts.

So far, we have investigated the interaction of CO_2 with small copper oxide, cobalt oxide and yttrium oxide clusters via infrared multiple-photon dissociation (IR-MPD) spectroscopy (collaboration with J. Bakker, FELIX laboratory). Clusters were produced by laser ablation of a metal target in the presence of He carrier gas seeded with O_2. Independent of the metal, cluster formation appears to be strongly charge dependent, with cations preferably forming oxygen-rich clusters, while anions tend to form stoichiometric and oxygen-deficient clusters. To study the cluster-CO_2 interaction, a CO_2/He mixture was subsequently introduced in an adjacent flow tube reactor and the resulting reaction products were investigated via infrared spectroscopy.

In the case of cationic copper and cobalt oxide complexes, the characteristic Fermi dyad of CO_2 is observed, indicating the presence of physisorbed, unactivated linear CO_2. In contrast, all anionic cluster complexes show bands which are characteristic for an activated bent CO_2 molecule (cf. Figure 1). Most interestingly, the IR-MPD spectra of yttrium oxide-CO_2 complexes appear to be more complex than the spectra of the copper and cobalt oxide complexes, potentially indicating different CO_2 binding motifs.
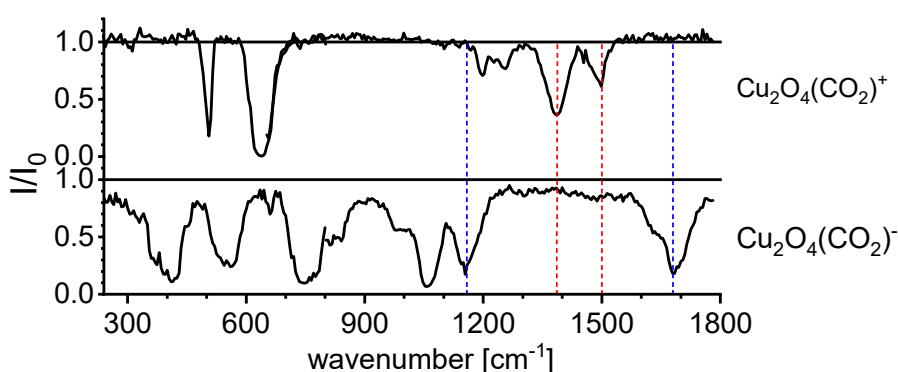

Figure 1: Comparison of IR-MPD spectra of a cationic and anionic $Cu_2O_4(CO_2)$ cluster complex. The red lines indicate the Fermi dyad, the blue lines indicate characteristic modes of an activated CO_2 molecule.

[1]   J. Artz, T.E. Müller, K. Thenert, J. Kleinekorte, R. Meys, A. Sternberg, A. Bardow & W. Leitner, Chem. Rev. **118(2)** (2018) 434-504.

[2]   https://www.catchy-etn.eu/

CO$_2$ and H$_2$ activation on zinc-doped copper clusters

Bárbara Zamora[1], László Nyulászi[1,2] and Tibor Höltzl[1,2,3]*

[1]Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, H-1111-Budapest, Műegytem rkp 3 Hungary
[2]ELKH-BME Computation Driven Chemistry research group H-1111-Budapest, Műegytem rkp. 3 Hungary
[3]Furukawa Electric Institute of Technology, Nanomaterials Science Group, H-1158 Budapest Késmárk utca 28/A, Hungary

Copper-based catalysts are commonly used to facilitate the CO$_2$ hydrogenation into useful chemicals. Here we systematically investigate the CO$_2$ and H$_2$ activation and dissociation on small Cu$_n$Zn$^{0/+}$ (n=3-6) clusters using Density Functional Theory. Our findings reveal that Cu$_6$Zn acts as a superatom, exhibiting an enlarged HOMO-LUMO gap and displaying inertness towards the activation or dissociation of CO$_2$ or H$_2$. While other neutral clusters exhibit weak CO$_2$ activation, with the exception of the otherwise unstable Cu$_4$Zn, the cationic clusters tend to preferentially bind CO$_2$ in a monodentate, non-activated manner. Generally, CO$_2$ activation is not favored. Conversely, H$_2$ dissociation is favored on all investigated clusters, except for Cu$_6$Zn.

We interpreted the bidentate CO$_2$ binding on the clusters based on the atomic charges and the energy decomposition analysis, which showed that the cluster donates electrons to the antibonding orbital of CO$_2$, thereby leading to its activation. In contrast to extended surfaces, the frontier orbitals of the clusters contribute mainly to the charge transfer. As the frontier orbital occupations and the orbital energies strongly depend on the number of itinerant electrons, CO$_2$ binding is also cluster-size dependent.
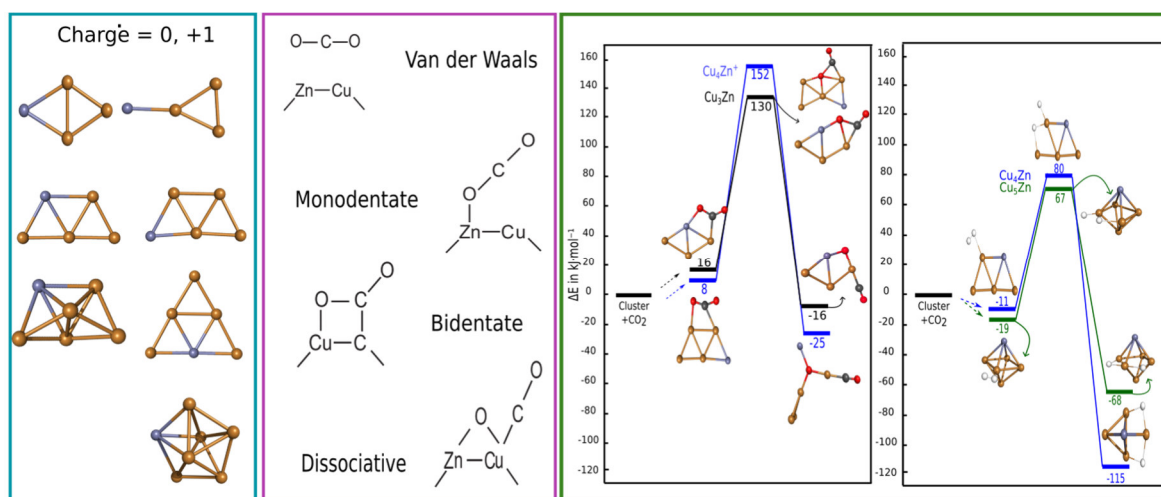

Figure 1: From left to right: Structural search of Cu$_n$Zn (n=3-6) clusters, CO$_2$ and H$_2$ binding modes, and the CO$_2$ and H$_2$ dissociation reactions mechanisms.

[1] Zamora, B. Nyulászi, L. Höltzl, T. CO$_2$ and H$_2$ activation on zinc-doped copper clusters. [Manuscript submitted for publication].

Chemical ordering of Au-Ni nanoparticles and their activities in oxygen reduction reaction

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Bimetallic catalysts play a significant role in conquering the activity volcano as a specific composition of metals tends to increase the yield and selectivity of the catalyst. Modelling bimetallic catalysts presents a challenge in determining the most-stable chemical ordering, which refers to the arrangement of atoms in the nanoparticle or surface. Precisely matching the surface structure and properties of experimentally synthesized materials in computational models is crucial and it requires complex task of identifying the most-stable chemical ordering from a multitude of possible arrangements. Here we present an improved Monte-Carlo-based method to determine the most-stable chemical ordering using a set of energetic descriptors obtained from an initial set of up to 30 different structures with typical chemical orderings. Initially, Au-Ni (431) kinked surfaces with 20:80, 40:60, 60:40, 80:20 Au:Ni ratios were simulated using this method. The most-stable structures were predicted to exhibit a core-shell arrangement (Ni-core, Au-shell). Subsequently, the effect of $1/4^{th}$ monolayer of oxygen and hydroxide on the corner, edge, and terrace descriptors was studied on the Au-Ni (431) kinked surface, revealing the migration of Ni atoms from the core to the shell under reaction conditions. The developed method was then applied to nanoparticles with four different compositions, once again predicting a core-shell arrangement, as depicted in Figure 1. Finally, to determine the chemical ordering and composition which shows high activity towards oxygen reduction reaction (ORR), we built (431) kinked surfaces and nanoparticles of various compositions using the obtained bare and OH-based energetic descriptors by performing Monte-Carlo at 300 K representing the reaction conditions. Based on the overall activity, one can choose a specific composition which better represent the surface arrangement of atoms for ORR at reaction conditions.
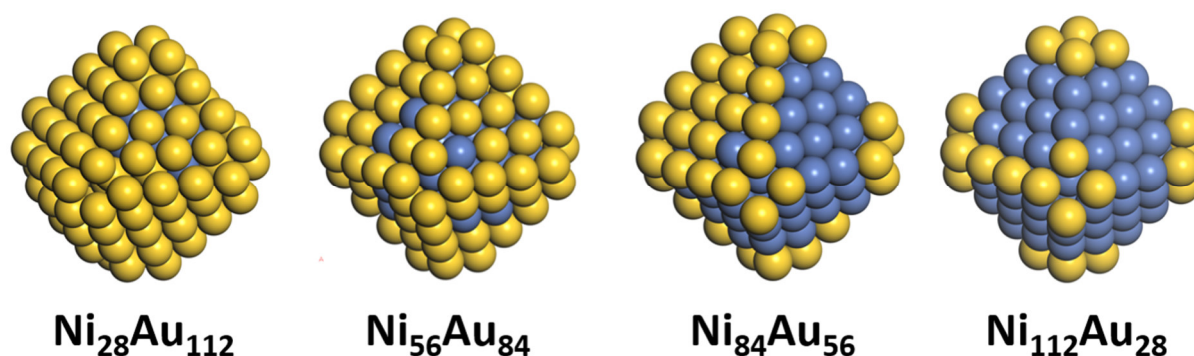

$Ni_{28}Au_{112}$ $Ni_{56}Au_{84}$ $Ni_{84}Au_{56}$ $Ni_{112}Au_{28}$

Figure 1: Most-stable chemical ordering of Au-Ni nanoparticles of different compositions

Gas-phase Pd and PdZn clusters deposited on ZnO and SiO$_2$ as model catalyst for CO$_2$ hydrogenation to methanol

Imran Abbas[1], Sumant Phadke[2,3], Joao Coroa[1,4], Jinlong Yin[4], Olga Safonova[2], Christophe Coperet[3], Didier Grandjean[1], Ewald Janssens[1]

[1]*Quantum Solid-State Physics, KU Leuven, Celestijnenlaan 200D, 3001 Leuven, Belgium*
[2]*Paul Scherrer Institute, Villigen PSI, 5232, Switzerland*
[3]*Department of Chemistry and Applied Biosciences, ETH Zürich, CH-8093 Zurich, Switzerland*
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Supported Pd nanoparticles have demonstrated promising catalytic activity for the hydrogenation of CO$_2$ into methanol, but the nature of the metal-support interface and its role in the reaction mechanism remains a topic of ongoing research [1-3]. In this study, we produced model catalysts by directly depositing well-defined Pd and PdZn clusters onto ZnO and SiO$_2$ powders using the Cluster Beam Deposition (CBD) technology. The clusters were deposited in high vacuum onto one gram of each pre-dried oxide powder placed in a vibrating cup to ensure the uniform deposition of size-controlled clusters containing 500 to 700 atoms. The cluster sizes were determined through in-situ time-of-flight mass spectrometry, and the loading of 0.1 wt% Pd clusters on the oxide powders was confirmed using ICP-OES. For the activity testing, the samples were in situ activated in pure hydrogen at 120°C for 30 minutes before conducting the catalytic tests. The catalytic activity tests for CO$_2$ hydrogenation were performed at 200-250°C and 40 bar, using 0.4g of each sample loaded in a plug flow reactor with a 5 mL/min feed gas mixture of 3H$_2$:1CO$_2$.

A very low concentration of Pd clusters (0.1 wt%) on ZnO was found to promote the hydrogenation of CO$_2$ to methanol and CO, while only minimal activity was observed for Pd/SiO$_2$. Fig. 1 illustrates a four-fold increase in the CO$_2$ hydrogenation rate compared to the sum of blank ZnO and Pd/SiO$_2$, confirming the excellent Pd-ZnO synergy in these model catalysts. To further investigate the Pd-ZnO synergy and uncover the structure-activity relationship, in-situ X-ray absorption spectroscopy was performed under CO$_2$ hydrogenation conditions. The use of well-defined Pd and PdZn catalysts enables a detailed investigation of the Pd-Zn and Pd-ZnO interfaces to unravel their structure-activity relationship.
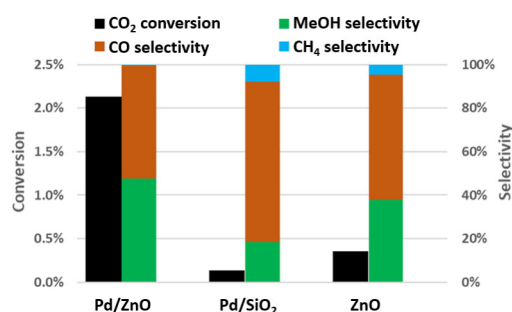

Fig: CO$_2$ conversion and product selectivity measured at 210°C and 40 bar of 3H$_2$:1CO$_2$ flowing at 5 mL/min.

[1] M. Zabilskiy, et al. *Angew. Chem. Int. Ed.* **2021**, 202, 17053–17059.
[2] S.R. Docherty et. al. *JACS Au* **2021**, 1, 450–458.
[3] H. Bahruji et al. *J. Catal.* ***2016***, 133–146.

Ultrafast wettability alteration: The decisive moments of adsorption on supported particles

Christian Weigelt[1], Mihai E. Vaida[2], Thorsten M. Bernhardt[1]

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[2] UCF Department of Physics, 4111 Libra Drive, Orlando, FL 32816-2385, USA

The detection of intermediate species during photoinduced surface chemical reactions and the ability to correlate their ultrafast dynamics with the morphology and electronic structure of the surface is crucial to fully understand and control photoinduced or photocatalytic reactions.

In this investigation, the ultrafast photodissociation dynamics of CH3Br molecules on variable size Au clusters grown on MgO/Mo(100) has been investigated using the pump-probe femtosecond-laser mass spectroscopy technique [1]. Collaborative photoemission investigations in conjunction with femtosecond extreme ultraviolet laser pulses are employed to sensitively detect the changes in the electronic structure of the Au clusters as they are grown on MgO/Mo(100) [2].

Further prospective research directions aim at the investigation of catalytic water splitting facilitated by supported manganese oxide clusters. In this respect, previous comparative gas phase catalytic model systems provide an extremely promising perspective [3].

[1] M. E. Vaida, T. M. Bernhardt: Tuning the ultrafast photodissociation dynamics of CH3Br on ultrathin MgO films by reducing the layer thickness to the 2D limit, Chem. Phys. Lett. 688, 106 (2017).
[2] M. E. Vaida, T. M. Bernhardt, T. Rawal, D. Le, B. M. Marsh, T. S. Rahman, S. R. Leone: Ultrafast photodissociation dynamics of CH3Br on MgO films decorated with variable size Au nanoparticles, to be submitted.
[3] S. Mauthe, I. Fleischer, T. M. Bernhardt, S. M. Lang, R. N. Barnett, U. Landman: A gas phase $Ca_nMn_{4-n}O_4^+$ cluster model for the oxygen evolving complex of photosystem II, Angew. Chem. Int. Ed. 58, 8504 (2019). S. M. Lang, N. T. Zimmermann, T. M. Bernhardt, R. N. Barnett, B. Yoon, U. Landman: Size, stoichiometry, dimensionality, and Ca-doping of manganese oxide based water-oxidation cluster catalysts: An oxyl/hydroxy mechanism for oxygen-oxygen coupling, J. Phys. Chem. Lett. 12, 5248 (2021).

Influence of the magnetic field configuration of a magnetron on the cluster growth mechanism in a sputtering gas aggregation source

João Coroa[1,2], Giuseppe Sanzone[1], Hailin Sun[1], Ewald Janssens[2], Jinlong Yin[1]
[1] Teer Coatings Ltd, West Stone, Droitwich, Worcestershire, WR9 9AS, UK
[2] Department of Physics and Astronomy, KU Leuven, B-3001 Leuven, Belgium

Cluster production using physical methods provides several advantages compared with chemical routes, such as better control of the size distribution and the minimised impact on the environment. On the other hand, their slow deposition rate has inhibited the physical approaches from being used more widely. To address this issue, we have systematically studied the influence of aerodynamics on the efficiency of cluster transportation in a cluster source [1]. Another important factor that needs to be considered is the influence of magnetic field configuration on the magnetron sputtering device.

In the 1980s, it was found that by tuning the unbalance degree of the magnetic field configuration, one can significantly increase the number of electrons escaping from the plasma sputtering region, increase the ion flux and the associated high ion bombardment on the substrate and thus produce very dense thin films [2]. Subsequently, simulations have been carried out to better understand how the unbalanced magnetic field influences the sputtering parameters [3].

Although significant progress has been made in the understanding of how the magnetic field influences the magnetron sputtering process, there are very few reports about its influence on cluster formation. An exception is a recent work by Vaidulych et al [4], where it is argued that a decrease in the magnetic field assisted with an increase in the flow of the carrier gas greatly improves the deposition rate of the nanoparticles. However, in this approach, the sputtering rates across experiments were not strictly maintained, which might influence the results in an unexpected way. Furthermore, a concrete explanation of how this magnetic field affects cluster growth is still missing.

In this work, preliminary simulation results on the influence of different magnetic field configurations are shown. The electromagnetic modelling software package OPERA was used to optimise the magnetic field configuration, and the configurations of the magnetic field on a magnetron were physically varied to validate the simulation results. Plasma density was measured at different magnetic configurations in an attempt to investigate its influence on the density of charged particles surrounding the target. A hypothesis will be proposed to explain cluster growth mechanisms under the influence of different plasma spatial distributions.

[1]   G. Sanzone, P. Lievens, Review of Scientific Instruments **vol. 92** (2021) p. 033901
[2]   B. Window, N. Savvides, Vacuum Science and Technology A Vacuum, Surfaces and Films **vol. 4** (1986) pp. 196 – 202
[3]   I. Svadkovski, S. Zavatskiy, Vacuum **vol. 68** (2002) pp. 283–290
[4]   M. Vaidulych, H. Biederman, Plasma Processes and Polymers **vol. 16** (2019) p. 08

A novel electrochemical cell for the *in situ* X-ray absorption spectroscopic investigation of cluster-based CO₂-electroreduction catalysts

Maximilian Winzely[1], Juan Herranz[1], Justus S. Diercks[1], Olga Safonova[1], Peter Rüttimann[1], Adam H. Clark[1], Paul Leidinger[1], Sumant Phadke[1], Thomas J. Schmidt[1,2]

[1] *Paul Scherrer Institut, CH-5232 Villigen, Switzerland*
[2] *Laboratory of Physical Chemistry, ETH Zurich, CH-8093 Zürich, Switzerland*

The electrochemical conversion of CO_2 into valuable products (e.g., CO or HCOOH) is a promising prospect to slow down global warming. While catalysts with a promising selectivity towards such C_1-products have been identified (e.g. Pd) [1], further improvements in their activity, selectivity and stability are needed. The required design of such improved catalysts can be greatly aided by recent advancements in the synthesis of mass-selected, (sub-) nanometric metal clusters by the so called cluster beam deposition (CBD) method and their subsequent characterization by *in situ* x-ray absorption spectroscopy (XAS).[2] However, constrains intrinsic to the CBD method limit the attainable catalyst loadings to ultra-low values $\leq 10~\mu g_{metal}/cm_{geom}^2$. This would in turn translate into unpractically long spectral acquisition times when performing *in situ* XAS measurements in a standard configuration (i.e., with an X-ray beam incidence of 45 or 90° with regards to the electrode plane). To tackle this problem we have developed a new spectroelectrochemical XAS flow cell that enables spectral acquisition in fluorescence mode using an X-ray beam incidence angle of $\leq 0.1°$ with regards to the working electrode's substrate plane, i.e., in a so called grazing incidence (GI) configuration (see Figure 1). In this acquisition configuration we successfully recorded an *in situ* spectrum of palladium in the metallic and full hydride state with a time resolution of 5 minute per spectrum while using a Pd-loading as low as $10~\mu g_{Pd}/cm^2$.
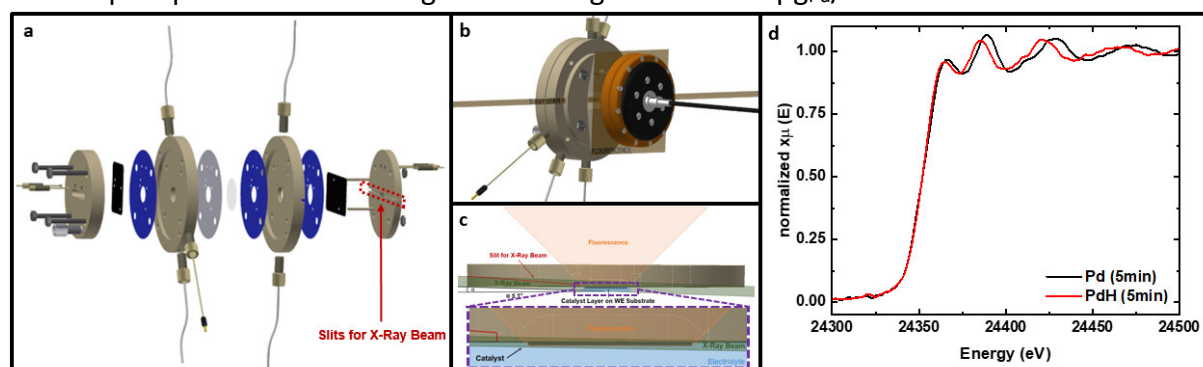

Figure 1: a) Technical drawing of the GIXAS cell assembly b) Experimental setup at the beamline including the GIXAS cell and fluorescence detector (represented as an orange disk) c) Detailed sketch of the outer working electrode part to visualize the grazing incidence of the X-Ray beam on the electrocatalyst. d) *in situ* XA-spectra of the Pd/C working electrode with a loading of $10~\mu g_{Pd}/cm^2$ polarized to the metallic and full hydride states (Pd vs. PdH, respectively) which were recorded within 5 minutes

[1]   J.S. Diercks, B. Pribyl-Kranewitter, J. Herranz, P. Chauhan, A. Faisnel, T.J. Schmidt, ournal of The Electrochemical Society 168 (2021) 064504.
[2]   A. Yadav, Y. Li, T.W. Liao, K.J. Hu, J.E. Scheerder, O.V. Safonova, T. Höltzl, E. Janssens, D. Grandjean, P. Lievens, Small **17** (2021) e2004541

High-Pressure Grazing Incidence Cell for *In Situ* XAS Characterization of Nanoparticles on Planar Substrates under CO$_2$ Hydrogenation Conditions

S. Phadke[1,2]*, J. Coroa[3,4], I. Abbas[4], J. Yin[3], D. Grandjean[4], E. Janssens[3], C. Copéret[2], O. V. Safonova[1]

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[2] *ETH Zürich, Vladimir Prelog Weg 1–5, CH-8093 Zürich, Switzerland*
[3] *Teer Coatings Ltd, Droitwich, Worcestershire, WR9 9AS, UK*
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Well-defined model catalysts studied under realistic CO$_2$-to-methanol hydrogenation conditions offer structure-activity insights, which enables a more profound understanding and a better design of methanol synthesis catalysts. In contrast to conventionally prepared catalysts, physical synthesis methods such as cluster beam deposition (CBD) can produce model nanoparticles of precise atomic structure and composition [1]. Depositing such nanoparticles on various planar substrates at very low metal loadings (0.1 – 10 µg/cm^2) provides an opportunity to understand particle size's effects and the catalyst's support on the reactivity. However, such model catalysts also present a challenge for *in situ* structural characterization using bulk-sensitive methods, such as X-ray absorption spectroscopy (XAS), since they are optimized for studying catalysts with about three to four orders of magnitude higher metal loading [2]. To address this, we have developed a grazing incidence (GI) *in situ* XAS cell that enables the study of the structure of these model catalysts under CO$_2$–to-methanol hydrogenation conditions at relevant temperatures and pressures.

We have successfully measured in situ XAS data for nanoparticles deposited on flat substrates using fluorescence detection. In particular, we obtained high-quality Pd K- and Au L$_3$-edge XAS data in 30-60 min for Pd and Ag$_{0.7}$Au$_{0.3}$ nanoparticles with ca. 2.5 – 10 µg/cm^2 loading at 230°C temperature and 20 bar pressure of reactive gases (CO$_2$:3H$_2$:Ar). With this proof-of-concept, we now intend to investigate innovative bimetallic systems produced by gas-phase cluster deposition and contribute to a rational design of CO$_2$ hydrogenation catalysts.

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Prospects and experimental challenges for matter-wave interferometry with massive metal clusters

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Almost a hundred years after the publication of Louis de Broglie's hypothesis, matter-wave interference experiments have shown the validity of the wave-particle duality for increasingly massive and complex systems. Recent experiments at the Long-Baseline Universal Matter-Wave Interferometer (LUMI) have shown interference of functionalized oligoporphyrins with masses above 25 *kDa* [1]. However, experiments with more massive objects are required to provide advanced tests of macroscopicity and wavefunction collapse models [2]. With this in mind, we turn to metal clusters to seek quantum interference of nanoparticles with masses up to 10^6 *Da*.

Here we present suitable source and detection schemes for interferometry experiments with yttrium and hafnium metal clusters [3]. A magnetron sputtering source is found suitable for the generation of a continuous metal cluster beam with a wide range of masses (80 - 800 *kDa*) and a small velocity distribution (v = 100 *m/s*, Δv/v < 10%). Yttrium and hafnium nanoclusters, whose ionization energies below 4.6 eV and photoionization cross-sections within the range of 10^{-14} to 10^{-15} *cm²*, are found to be compatible with the use of photoionization gratings and detection with 1 *W* of 266 *nm* UV laser light focused to 40 x 500 *μm²*.

We present some of the open technical challenges. Special emphasis is made on the alignment criteria for angular and translational degrees of freedom of all light gratings [4], the vacuum requirements, and vibrational isolation mechanisms. We discuss how each of these challenges is being addressed in the laboratory to push the limits of quantum interference.
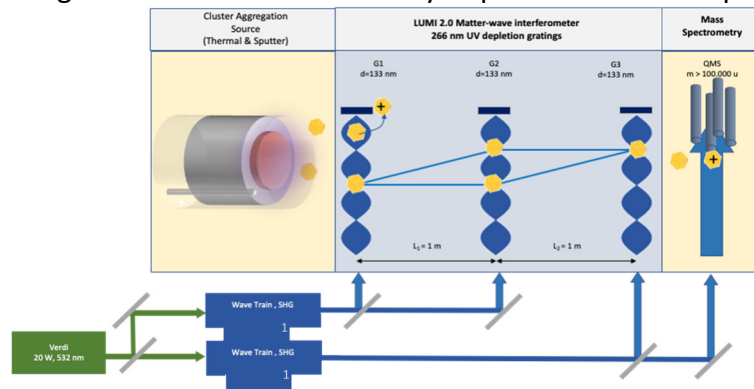

Figure 1: Current setup of the LUMI 2.0 matter-wave interferometer. Left to right: magnetron sputtering source, 266 nm standing light wave gratings, and mass filtered photoionization detector.

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Surface Modulation on Au$_{25}$(SR)$_{18}$ NCs *via* the Ligand Exchange Induced Size/Structure Transformation

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Fundamental understanding of the structure-property correlations and the rational design of nanoclusters (NCs) has been a long-held aspiration in the field of nanoscience. To a great extent, transformation chemistry can be utilized in this regard to understand the structural growth patterns and corresponding property evolutions in atomically precise metal NCs.[1,2] Therefore, understanding the transformation mechanism is of paramount importance to functionalize and tailor the surface properties and achieve rational synthesis and design of NCs. Ligand exchange induced size/structure transformation (LEIST) is a common transformation methodology where a precursor NC is thermally activated in presence of an excess amount of exogenous thiol to undergo size/structure transformation.[3] The LEIST methodology can thus be employed to impart specific properties to the NCs by modifying the surface ligands. Herein, we have carried out a comparative study on LEIST of [Au$_{23}$(S-*c*-C$_6$H$_{11}$)$_{16}$]$^-$ NCs using the *p*-XC$_6$H$_4$SH, X = F, Cl, Br, and H under thermal conditions. We have tuned the electronegativity at the para position of the incoming benzenethiols and tried to understand the changes in the transformation products as well as mechanism with this slightest change in the incoming thiol structure. Time-dependent UV-vis spectroscopy and MALDI-MS spectrometry were employed to monitor the transformation process and both revealed the formation of [Au$_{25}$(*p*-XC$_6$H$_4$S)$_{18}$]$^-$ NCs, X = F, Cl, Br, H. Single crystals of the as-obtained NCs revealed the structural similarity of the [Au$_{25}$(*p*-XC$_6$H$_4$S)$_{18}$]$^-$ NCs to the previously reported Au$_{25}$ NCs.[4] However, the [Au$_{25}$(*p*-BrC$_6$H$_4$S)$_{18}$]$^-$ NCs showed an inconsistency in the transformation mechanism and the photophysical properties compared to the [Au$_{25}$(*p*-XC$_6$H$_4$S)$_{18}$]$^-$ NCs, X = F, Cl, H. Further the ultrafast transient absorption spectroscopy was employed for in-depth understanding of the varying electronic effect of incoming thiols on the transformation mechanism as well as product formation.
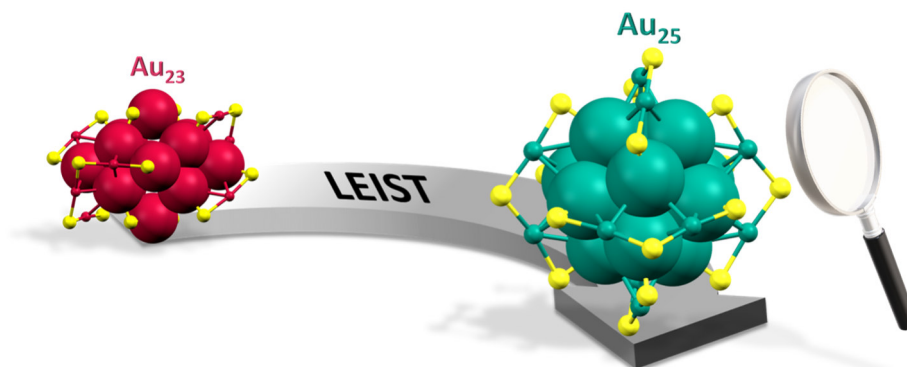

Figure 1: Detailed investigation into the LEIST of Au$_{23}$(SR)$_{16}$ NCs to Au$_{25}$(SR')$_{18}$ NCs

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Correlating the Impact of Heteroatoms Core-Tailoring of Atomically Precise $Ag_{25}(SR)_{18}$ Nanoclusters on the Photocatalytic Activities

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Research on the anisotropic structures of nanomaterials has expanded the fundamental understanding of their structure-property relationships, whereby a wide range of applications have been developed. Herein, we go deeper into this relationship by studying the electronic properties and photocatalytic activities of the atomically precise $Ag_{25}(SR)_{18}$ nanoclusters. The central metal atom in an atomically precise Ag_{25} nanocluster (NC) is replaced with a single Pd, Pt, and Au atom, respectively, and employed as a model system to study the structure–property–activity relationship at the atomic level. While the geometric structures are well-preserved after doping, the electronic structures of Ag_{25} NCs are significantly altered. Results show that heteroatoms doping has a negative impact on performance, particularly in the cases of Pd and Au doping. Ultraviolet photoelectron spectroscopy measurements and density functional theory calculations suggest that the lower activities are due to an energy mismatch between the levels of doped NCs and TiO_2. [1, 2] These findings not only reveal the impact of heteroatoms doping on the electronic properties and photocatalytic activities of NCs, but can also guide the design of heterometallic NCs for photocatalytic applications.
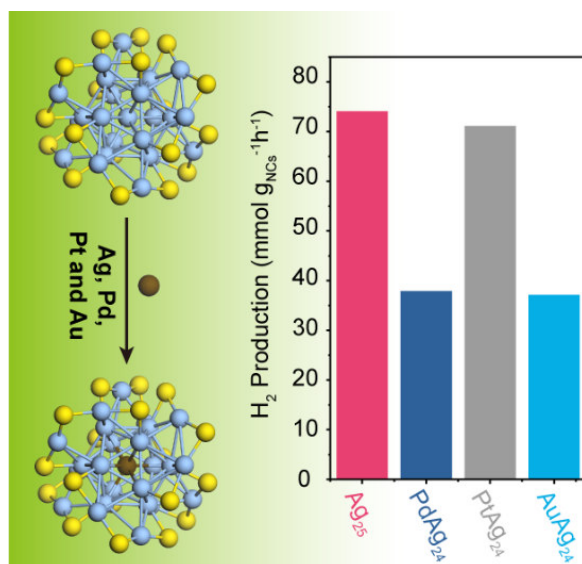

Figure 1: Schematic illustration of the photocatalytic activities of $MAg_{24}(SR)_{18}$ nanoclusters

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Evaluation of Superatomic Electronic Structures of Ligand-Protected Gold/Silver Superatoms by Gas-Phase Photoelectron Spectroscopy

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Ligand-protected gold/silver clusters have gathered much interest as new functional nanomaterials [1]. High stability of a benchmark system $[Au_{25}(PET)_{18}]^-$ (PET = 2-PhC_2H_4S) with an icosahedral Au_{13} core has been explained by the electronic shell closure of superatomic orbitals with $(1S)^2(1P)^6$ configuration [2]. Such a superatom concept has been applied to rationalize the doping effect on the electronic structure of $[MAu_{24}(PET)_{18}]^-$ and the bonding scheme in a bi-icosahedral Au_{23} core of $Au_{38}(PET)_{24}$ [3]. We have elucidated superatomic electronic structures of ligand-protected Au/Ag superatoms by gas-phase anion photoelectron spectroscopy (PES) (Figure 1a [4]).

Free anions of ligand-protected superatoms were produced by an electrospray ionization source, mass-selected by a time-of-flight mass spectrometer, and irradiated with a UV pulsed laser in a magnetic-bottle type photoelectron spectrometer for PES. PE spectra of $[M_{25}(SR)_{18}]^-$ (M = Au, Ag) (Figure 1b [5]) demonstrated that the corresponding neutrals have large electron affinities comparable to those of halogen atoms and thus they can be categorized as superhalogens [6]. PES on $[MAg_{24}(SR)_{18}]^-$ (M = Ag, Au, Pd^-, Pt^-) (Figure 1b [5]) revealed that the doping of Pd/Pt at the central position upshifted the energy levels of 1P superatomic orbitals, which can be explained by the two-step jellium model [8]. The PE spectra of $[MAu_{37}(PET)_{24}]^-$ (M = Pd, Pt) (Figure 1c [7]) with bi-icosahedral MAu_{22} cores exhibit two distinct peaks at the spectral onset, which are assigned to molecular orbitals constructed by bonding and antibonding interaction between the 1P superatomic orbitals of Au_{13} and MAu_{12} [3].
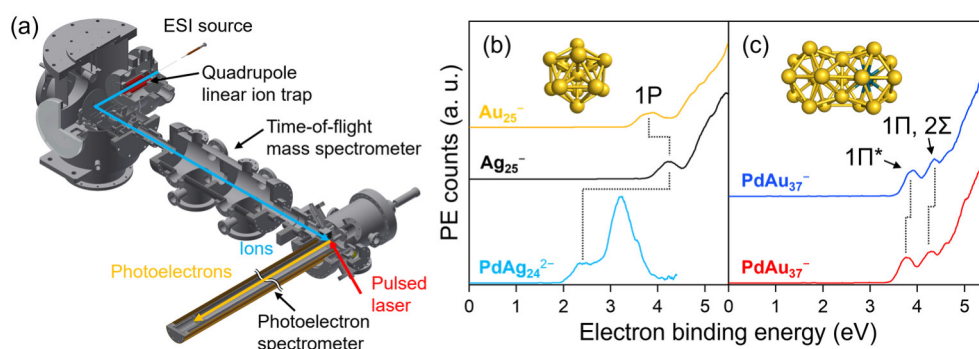

Figure 1: (a) Schematic view of the apparatus. PE spectra of (b) $[Au_{25}(PET)_{18}]^-$, $[Ag_{25}(DMBT)_{18}]^-$, a $[PtAg_{24}(DMBT)_{18}]^{2-}$ and (c) $[MAu_{37}(PET)_{24}]^-$ (M = Pd, Pt). The inset shows the structures the cores.

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π-π Interactions in Host-Guest Complexes
Revealed by Cryogenic Ion Mobility-Mass Spectrometry

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Crown ethers play an important role in the field of host-guest chemistry owing to their ability to encapsulate the guest ions efficiently and selectively. We previously studied the conformations of dibenzo-24-crown-8 (DB24C8) (Fig. 1a) complexes with alkali metal ions using ion mobility-mass spectrometry (IM-MS) and confirmed the coexistence of two conformers, closed and open [1]. In Na^+(DB24C8), the abundance ratio of the conformers was closed:open = 0.25:1 at 86 K [1]. In dinaphtho-24-crown-8 (DN24C8) (Fig. 1b), it is expected that the closed conformer should be more strongly stabilized due to the stronger π-π interactions between aromatic rings. In this study, conformers of DN24C8 complexes with Na^+ and K^+ ions were separated by cryogenic IM-MS, and their structures were identified to investigate the effect of π-π interactions on guest ion recognition by crown ethers.

Gas-phase metal ion-crown ether complexes were sampled by electrospray ionization (ESI) method using methanol solutions of DB24C8 or DN24C8 and inorganic salt (NaCl, KCl). Ions were then delivered to a cryogenic ion drift tube for conformer separation and mass-analyzed by a reflectron-type time-of-flight mass spectrometer. We performed all IM-MS experiments under the presence of He buffer gas in the ion drift tube. By evaluating the drift velocity in the drift tube, we determined the experimental collision cross section (CCS) for each complex. Using quantum chemical calculations, both theoretical CCSs and relative energies were obtained for candidate structures. Conformations of the complexes were assigned by comparing the experimental and theoretical CCSs, in addition to the consideration of the stabilities of the candidate structures.

As a result, two types of conformers, closed and open, were separately observed at 86 K (Fig. 1c,d). These two conformers have different distances between the two naphthalene rings of the DN24C8. The abundance ratio of the conformers was closed:open = 1:0.15 at 86 K for Na^+(DN24C8). Namely, the relative abundance ratio of the closed conformer was larger than that for Na^+(DB24C8). In the quantum chemical calculations visualizing the extent of the π-π interactions, DN24C8 complexes were found to have wider regions of π-π interactions than the DB24C8 complexes. Therefore, the closed conformations were concluded to be predominant for the DN24C8 complexes due to the stronger π-π interactions.
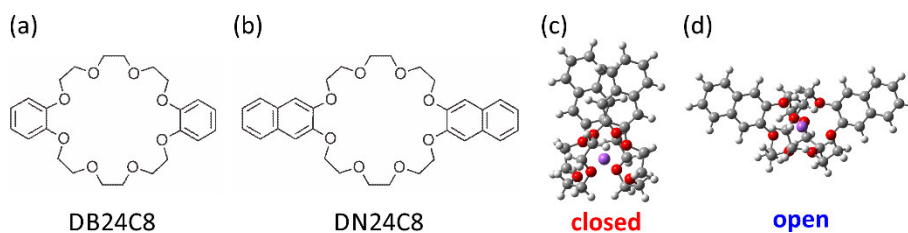

Figure 1: Formulas of (a) DB24C8 and (b) DN24C8, and stable structures of (c) closed and (d) open conformers of Na^+(DN24C8) calculated at the M05-2X/6-311++G(d,p) level of theory.

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Size dependent structures of platinum oxide cluster cations and anions studied by ion mobility-mass spectrometry

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Platinum clusters are potential candidates for new redox catalysts because bulk-phase platinum is widely used as such catalysts. For instance, Pt_{19}^- is a promising candidate as a catalyst to promote O_2 reduction reactions forming H_2O in fuel cells because of the higher reactivity of Pt_{19}^- than that of bulk-phase or nanosized Pt [1]. Atomic-level structures of clusters are essential factors for size-dependent catalytic activities. Thus, it is vital to elucidate how cluster structures change with size for utilizing clusters as novel redox catalysts. Structures of gas-phase metal oxide clusters provide a model for understanding the detailed mechanism of redox reactions catalyzed by the clusters, such as the dynamics of O atoms through reactions. In this study, we revealed the structures of platinum oxide cluster cations and anions ($Pt_nO_n^{+/-}$) depending on their sizes (n = 4–7) by using ion mobility-mass spectrometry combined with quantum chemical calculations [2]. $Pt_nO_m^{+/-}$ cluster ions were generated by laser vaporization of Pt in the presence of O_2 mixed in the carrier gas. The generated cluster ions were injected into an ion-drift cell, where collision cross sections (CCSs) of the clusters with He atoms were measured. The ions which exited from the ion-drift cell were analyzed by mass spectrometry. Candidate structures and energies of the $Pt_nO_n^{+/-}$ cluster ions were obtained by DFT calculations (B3LYP/Pt: SDD, O: 6-311+G(2d)). Geometrical structures of the ions were assigned by comparison of the experimental CCSs with the theoretical values. The observed cluster ions had predominant compositions of $n:m$ = 1:1 both for cations and anions. The CCSs of $Pt_nO_n^{+/-}$ increased monotonically with the cluster size for n = 4–7, as shown in **Fig. 1**. For the cluster cations, $Pt_4O_4^+$ was assigned to a planar structure from its CCS. For n = 5 and larger $Pt_nO_n^+$, the experimental CCSs agreed better with three-dimensional structures than with planar isomers. Thus, the structures of cationic $Pt_nO_n^+$ change from planar to three-dimensional structures at n = 5. On the other hand, theoretical CCSs of planar structures in anionic $Pt_nO_n^-$ consistently agreed with the experimental results for n = 4–7. These results suggest that $Pt_nO_n^-$ anions prefer bulky planar structures compared to $Pt_nO_n^+$ cations.
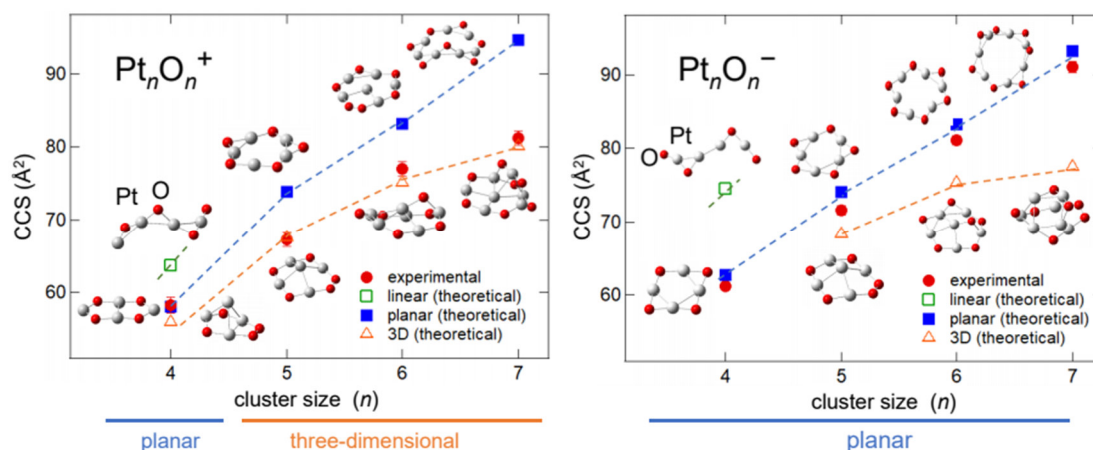

Figure 1: Experimental and theoretical collision cross sections (CCSs) of $Pt_nO_n^{+/-}$.

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Effect of nanoparticle size on Boron-Doped Transition Metals

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Through the reduction of metal salts with borohydride, boron can be incorporated into transition metals. The profound influence of boron on the catalytic properties of surfaces, such as Pd and Pt, has been well-established. However, the geometric, electronic, and energetic properties of boron-doped systems have not been studied systematically. In this study, we delve in the thermodynamics and kinetics involved in the incorporation of boron into both 1.5 nm nanoparticles (NPs) and extended (111) surfaces of various metals including Ir, Rh, Ni, Pd, Pt, Cu, Ag, Au, and Al by using Density Functional Theory (DFT) calculations. The results revealed stability of boron atoms within interstitial subsurface positions in Rh, Pt, and Pd (111) surfaces. The presence of low coordination sites within NPs enhances the diffusion towards subsurface sites, leading to the emergence of in-surface sites that are not typically observed on (111) surfaces. Notably, these specific locations were observed to exhibit exceptional thermodynamic stability, particularly in Rh, Ir, and Ni NPs. In contrast to the extended surfaces, the barriers for boron migration from adsorption sites to in-surface and subsurface positions were calculated to decreased to < 1 eV on terrace sites and < 0.4 eV on edge sites on all NPs except Ir, as shown in Figure 1. The incorporation of boron led to a notable shift in the d-band center of neighboring metal atoms towards Fermi level, amounting to approximately ~0.5 eV. The significant alteration in electronic properties provides a compelling explanation for the substantial impact of boron on the catalytic activity of transition metal catalysts.
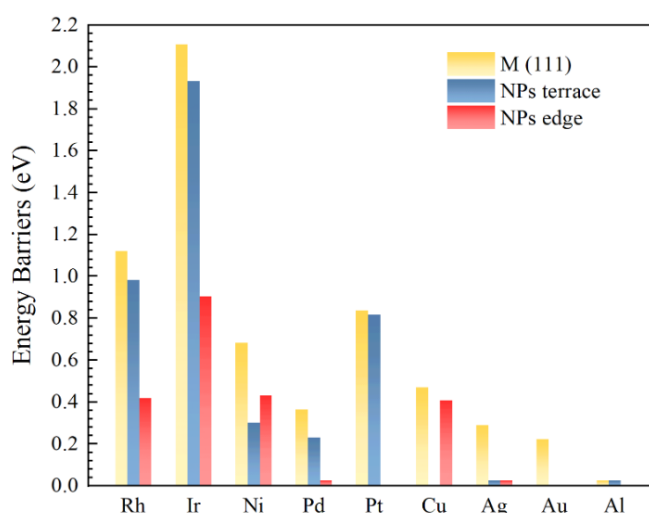

Figure 1: Gibb free energy barriers for the migration process of one boron atom on metal {111} surface and M_{140} nanoparticle at 298 K

X-ray induced explosion dynamics of methane clusters

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Short wavelength free-electron lasers (FELs) enable the investigation of individual nanometre-sized particles, such as viruses or large biomolecules, via single-shot coherent diffractive imaging [1]. However, the intense X-ray pulses needed for single-molecule imaging also lead to ultrafast radiation damages, thus limiting the achievable resolution [2]. Several studies have been carried out to investigate possible energy dissipation pathways which preserve the scattering-relevant structure upon excitation [3-5]. In this context, hydride compound systems, i.e. methane or ammonium clusters serve as model systems for bio-molecules. Under certain conditions these systems eject fast protons, thus taking away excess charge and energy. This "proton boost" has been predicted to preserve the system's backbone [5]. In our experimental study, we investigate the dissociation dynamics of methane clusters upon irradiation with intense FEL pulses. Using ion spectroscopy methods, we investigate the conditions for fast protons in the range of photon energy and FEL intensity relevant for single particle imaging. Our analysis shows that protons indeed massively dominate the spectra in a certain intensity regime. However, the protons' mean kinetic energy is highest in another intensity range, where the yields of hydrogen and heavier ions are close to their stoichiometric distributions in the cluster. Our results can be explained in the picture of the transition from Coulomb explosion to hydrodynamic expansion. We find that the Coulomb explosion of a heterogeneous system leads to massive segregation and the disproportionate acceleration of the light ions, while the hydrodynamic expansion developing at the edge of the cluster does not favour strongly one of the species. In particular, towards the highest focal intensities, as needed for single particle imaging, our observations show that the proton boost does not play a relevant role in the ion dynamics.

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Chemical Reactivity of Boron Substituted Aluminum Superatoms on Organic Substrates

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Nanoclusters are promising building blocks for functional nanomaterials due to their high designability which could control the material properties by tuning constituent elements and number of constituent atoms. Among them, there is a specific class of nanoclusters so called ''superatoms'' exhibiting high chemical stability in gas phase, which satisfy both an electron shell closure of superatomic orbitals and a geometrically packed structure. Aluminum 13-mer anion ($Al@Al_{12}^-$) is one of the most representative superatoms which shows high chemical stability in gas phase based on 40 electron shell closure of 2P superatomic orbitals and icosahedral (I_h) structure. When the central Al atom is replaced by a smaller and homologous boron (B) atom, the $B@Al_{12}^-$ superatom exhibits higher stability because of relaxing the strains of Al_{12} cage while maintaining 40 electron shell closure [1]. The substitution with homologous elements enables us to design geometric structures and electron density distributions, while keeping total number of valence electrons.

To utilize such superatoms as functional nanomaterials, it is required to achieve surface decoration with the superatoms optimized physically and chemically, and to evaluate the stability in condensed phase. Recently, it has been revealed that Al_n^- (n=7-24) and $Al_{12}B^-$ could be stabilized on a surface pre-decorated by a *p*-type organic molecule of hexa-*tert*-butyl-hexa-*peri*-hexabenzocoronene (HB-HBC; $C_{66}H_{66}$) [2]. In this study, Al_nB^- (n=6-14) was deposited on a HB-HBC decorated substrate, in which the reactivity of Al_nB was evaluated by combining x-ray photoelectron spectroscopy (XPS) and oxygen molecule exposure defined by Langmuir (1 L = 1.33×10^{-3} Pa$\times$1 s).

XPS (Mg Kα: $h\nu$ = 1253.6 eV) spectra were measured around Al 2p and O 1s core levels for Al_n (n=7-15) and Al_nB (n=6-14) immediately after deposited on the HB-HBC substrates at 0.6 ML equivalent. For pure Al_n (n=7-15) deposited on the HB-HBC substrate, a sharp Al 2p peak was observed at a binding energy of 73 eV in all sizes, where the energy position for metal Al (Al^0), while O 1s signal was hardly observed. On the other hand, for Al_nB on the HB-HBC substrates, the Al 2p XPS shows a size-dependent change from a sharp Al^0 peak to a broad peak observed at 75-76 eV, where almost the same energy with Al oxide (Al^{3+}). In fact, O 1s signal was increased with the decrease of size from n=12. For Al_6B, the Al 2p peak appeared as almost one oxidized component of Al^{3+} despite immediately after deposition. Therefore, small Al_nB nanoclusters are highly activated by B atom substitution even with the deposition on HB-HBC substrate. To quantitatively estimate a reactivity, the relative reactivity of Al_{n+1} and Al_nB based on that of $Al_{12}B$ was evaluated from the decrement of Al^0 component in Al 2p with oxygen molecule exposures. For size of n less than 11, the relative reactivity of Al_nB was 3 to 20 times higher than that of Al_{n+1} which is the same number of constituent atoms. On the other hand, for n larger than 12, the relative reactivity of Al_nB was equal to or less than that of Al_{n+1}, indicating nanoclusters were chemically stabilized by forming icosahedral Al_{12} cage, overcoming the activation effect of B atom.

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Characterization of Pyrrole Dimer Cations and Their Solvated Clusters by IR Spectroscopy

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Aside from π H–bonding, cation/anion–π, and π–π stacking interactions, the charge resonance (CR) is a fundamental and very strong force in charged arene dimers [1]. In aromatic dimer cations, the positive charge is shared between the molecules depending on their ionization energy (IE) differences. Because of the charge resonance interaction between the monomers, a splitting between the two electronic states results in the charge resonance band due to the coupling of those electronic states. Even though the charge resonance interactions have been studied extensively over the years, only a rough estimation of the asymmetry in the charge distribution in the dimer is possible because of the broadness of the CR transition.

To this end, we previously demonstrated a new high–resolution experimental approach (infrared photodissociation spectroscopy (IRPD)) to precisely probe the charge distribution and the CR interaction in aromatic dimer cations for the prototypical case of the pyrrole dimer cation (Py_2^+). Py (C_4H_5N) is a five-membered heterocyclic ring which has a single isolated and uncoupled NH stretch oscillator whose frequency is strongly dependent on its charge state [1-3]. However, due to the finite width of the free NH stretching peak in the IRPD spectrum of Py_2^+, the structural isomers of Py_2^+ are not easily and directly distinguishable (Figure 1). Therefore, herein we characterize Py_2^+ by IRPD and dispersion-corrected density functional theory calculations (B3LYP-D3/aug-cc-pVTZ) depending on the formation methods and internal temperature of the dimer cation. Analysis of IRPD spectra of mass-selected Py_2^+ and its cold Py_2^+–Ar and Py_2^+–N_2 clusters combined with geometric parameters of intermolecular structures and binding energies provides a clear picture of the pyrrole dimer structures.
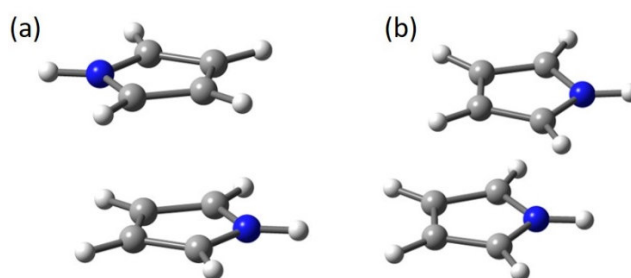

Figure 1: Optimized isomers of Py_2^+ at the B3LYP-D3/aug-cc-pVTZ level (a) antiparallel and (b) parallel

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Electronic state of a bis(μ-oxo) di-manganese oxide cluster revealed by XAS and XMCD

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The oxidation and spin states of the $CaMn_4O_5$ cluster of oxygen-evolving complex are crucial for understanding dioxygen formation in the Kok cycle. In particular, the S_4 state is notoriously difficult to model or to observe because of the millisecond time scale of the S_3-S_0 transition [1]. Two competing models for the S_4 state, responsible for O_2 formation, exist [2] that feature distinctively different oxidation states of +4 and +5 of the manganese atom at the reaction site. Despite the fact that the spin states of the manganese atoms in state S_4 are still under debate, the reactivity of the $CaMn_4O_5$ cluster is believed to be spin-dependent [3].

In this work, we report on the characterization of gas-phase manganese oxide complexes via X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD), measured in ion yield mode at the manganese $L_{2.3}$-edge on a series of cryogenically cooled, mass-selected manganese oxide ions [4]. We identify oxidation and spin states by comparison with XAS and XMCD spectra of reference manganese compounds with known oxidation states, in combination with multireference calculations.

Our most important result is the identification of a bis(μ-oxo) bridged dimanganese oxide species with manganese(V) in a high-spin state. This is the first observation of the elusive manganese(V) high-spin state in a polymagnanese oxido complex [5,6, 7]. The observed result might have implications for the oxidation and spin states of the $CaMn_4O_5$ complex in the S_4 state.

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Magnetic deflection of sodium doped solvent clusters

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Since the discovery of concentration-dependent colors of alkali metal-ammonia solutions in the early 19th century [1], excess electrons in alkali metal solutions have been found to be important in many areas. They are ubiquitous in liquid-phase chemistry [2] and play an essential role in chemical reactions [3] and biology [4]. Extensive experimental and theoretical work has been performed on solvated electrons in alkali metal solutions [2] (and references therein). However, the underlying correlation effects of solvated electrons are still not well understood. While magnetic measurements have probed such effects on alkali metal solutions [5, 6], diamagnetic and paramagnetic species have not yet been identified in such bulk phase experiments [2].

We present a study of the magnetic properties of sodium-doped solvent ammonia, water, dimethyl ether, and methanol clusters ($Na(Solv)_n$, n=1-4) [7, 8]. Using a pulsed Stern-Gerlach deflector, we measure the magnetic deflection of a neutral cluster beam using both Velocity Map and Spatial Map Imaging detection. The experimental deflection is compared with molecular dynamics simulations based on the Zeeman interaction of a free spin ½ system.

The comparison reveals unperturbed magnetic properties of a spin ½ system for both $NaNH_3$ and NaH_2O. All other studied clusters $Na(NH_3)_n$ (n=2-4), $Na(H_2O)_n$ (n=2-4), $Na(DME)_n$ (n=1-3) and $Na(MeOH)_n$ (n=1-4), by contrast, show reduced deflection compared with that of a spin ½ system. These deviations from a spin ½ behavior are attributed to intra-cluster spin-relaxation effects occurring on time scales similar to or faster than the experiment. Determining spin relaxation times for these systems allows us to identify experimental trends in their magnetic behavior. These trends are discussed in terms of spin-vibrational coupling of thermally accessible rovibrational eigenstates.

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Magnetism of single-doped paramagnetic tetrel clusters studied by Stern-Gerlach experiments: Impact of the diamagnetic ligand field and paramagnetic dopant

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The magnetic behavior of clusters results from a complex interplay of geometric and electronic structure and is therefore closely linked to the chemical bonding between the atoms involved. In order to gain a better understanding of magnetism and thus chemical bonding, diamagnetic tetrel clusters were alloyed with a paramagnetic dopant. In this way, on the one hand, the influence of the diamagnetic tetrel ligands on the magnetism can be studied in detail and, on the other hand, it can be followed how the paramagnetic defect influences the chemical bonding in nanoclusters.

For this purpose, Stern-Gerlach experiments were carried out on clusters of the type MSn_N (M = Mn, Fe; N = 11, 12, 14, 17). By varying the nozzle temperature of the laser vaporization cluster source, the thermal excitation, in particular of the vibrational degrees of freedom, can be changed in a controlled manner. At low temperatures, i.e. when a large part of the clusters is in the vibrational ground state, often super-atomic behavior can be observed. [1] In contrast, at high nozzle temperatures, i.e. when the vibrations of the clusters are thermally excited, spin relaxation takes place in the magnetic field and an exclusively one-sided deflection of the cluster beam is observed. [2] This deflection results from the average magnetic dipole moment $\bar{\mu}_z$ of the cluster ensemble with respect to the external magnetic field B_z. It turns out that the value of $\bar{\mu}_z$ can vary by more than an order of magnitude if only the number of diamagnetic tetrel atoms is changed. For example, the $MnSn_{17}$ cluster is more than 15 times more magnetic than the $MnSn_{14}$ cluster.

The analysis of the temperature dependence of $\bar{\mu}_z$ can be used to determine $g^2S(S+1)$ so that possible combinations of the electronic g-factor and the spin multiplicity S are obtained. Since the g-factor can be unambiguously determined from the occurrence of the super-atomic behavior at low temperatures, a consistent picture of the magnetic behavior of the clusters appears. Deviations of the g-factor from the free electron value are due to additional orbital contributions to the magnetic moment. [3] Based on relativistic quantum chemical calculations, the g-factors can be related to the geometric and electronic structure of the clusters. This makes it possible to understand in detail the experimentally observed magnetic behavior when the number of tetrel atoms is varied or when the paramagnetic dopants are exchanged.

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Abstracts

Searching for the Origin of Magic Numbers Amongst Sodium Chloride Clusters

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As one of the main components of sea salt aerosols, sodium chloride is involved in numerous atmospheric processes such as cloud formation and photochemical as well as chemical reactions, significantly affecting the climate on Earth. [1] Gas phase clusters are ideal models to study fundamental physical and chemical properties of sodium chloride. According to previous studies [2], these properties are significantly affected by the cluster size. Of particular interest are magic cluster sizes, which exhibit high intensities in mass spectra.

In order to understand this size dependency, we performed a combined experimental-theoretical study, focusing on the relative stability as well as their dissociation behavior. In contrast to earlier studies [3], our calculations show that the binding energy of a single NaCl unit or the respective ion (Na^+ or Cl^-) to the smallest anionic $(NaCl)_xCl^-$ and cationic $(NaCl)_xNa^+$ magic cluster with $x = 4$ is lower than that of the neighboring cluster sizes and thus cannot be the reason for the special stability.

Sustained off-resonance irradiation collision-induced dissociation (SORI CID) experiments performed in a Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS) reveal, that the loss of neutral clusters $(NaCl)_x$ with even x (especially $x = 2$ and $x = 4$) is in most cases more favorable than the loss of single NaCl units, as assumed so far [2]. This can be explained by the calculated high stability of neutral clusters $(NaCl)_x$ with even x, whose minimum energy structures are cubic, resembling the sodium chloride crystal lattice.

Analysis of the density of states as well as the Rice-Ramsperger-Kassel-Marcus (RRKM) rates for the anionic and cationic magic cluster with $x = 4$ and the neighboring cluster sizes with $x = 3$ and $x = 5$ yields an explanation for the high stability of the smallest magic clusters. Our findings emphasize the importance of considering the kinetics of the cluster dissociation, not only the respective energetics.

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Photochemistry of Pyruvate Embedded in Sea Salt Clusters

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Marine aerosol is one of the most important naturally occurring aerosol systems, due to the large coverage of Earth's surface by the ocean. Aerosols in general have a great influence on Earth's climate through their direct and indirect interaction with solar radiation. Besides inorganic salts such as sodium chloride, also organic material such as acids, terpenes, lipids and saccharides are incorporated in marine aerosols. Through the exposure to sunlight, these organic materials can undergo photochemical processing and, as a consequence, they can produce highly reactive species, for example $OH^{\cdot}$ radicals. Pyruvic acid is one of the most abundant α-carboxylic acids in the atmosphere. In this work, the photochemistry of pyruvate in a salt environment has been investigated. Previous work on the photochemistry of glyoxylate has shown that the acid undergoes photolysis leading to non - stoichiometric fragments that incorporate a $CO_2^{\cdot-}$ radical anion [1]. In this work, we investigate whether other acids also undergo a photolysis process, when embedded in a salt environment, or if glyoxylate is a special case.

All spectra for this work were recorded using a 9.4T FTICR mass spectrometer and a UV/VIS OPO laser system. The measured wavelength range lies between 210 and 400 nm, including the environmentally relevant actinic region from 290 - 400 nm. In total, two systems were measured, one being pure sodium pyruvate clusters $Na_n(CH_3COCOO)_{n-1}^+$, n = 4,5 and the other one being sodium chloride clusters where one chloride ion is substituted by pyruvate $Na_nCl_{n-2}(CH_3COCOO)^+$, n = 4 - 8. For two cluster sizes in the sodium chloride system and for both pure sodium pyruvate clusters, non - stoichiometric fragments were observed. However, despite the fact that photolysis is the main degradation pathway in the atmosphere for pyruvic acid [2], only traces of this phenomenon could be found in the experiments conducted here. This suggests that the salt environment suppresses the photolysis.
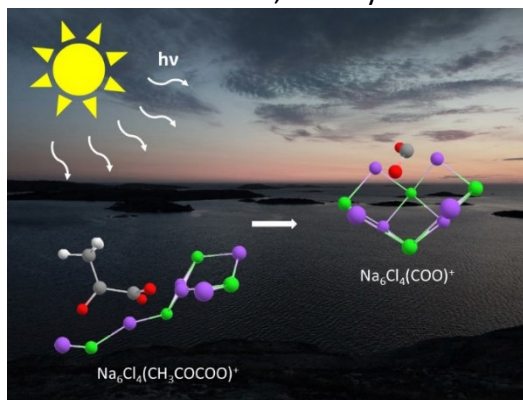

Figure 2: Artistic representation of the pyruvate photolysis

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Blackbody infrared radiative dissociation and master equation modelling of hydrated peroxycarbonate radical anions

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If molecular clusters are stored for several seconds under ultra-high vacuum conditions, dissociation due to ambient blackbody radiation can be observed. Thereby, absorption of blackbody infrared photons leads to vibrational excitation and eventually to dissociation of the cluster (see Figure 1). This process, known as blackbody infrared radiative dissociation (BIRD), can be simulated with master equation modelling, predicting temperature dependent dissociation rates for given dissociation energies. By comparing rates from master equation modelling with experimental rates, dissociation energies of the molecular clusters can be determined. For reliable energetics, however, the temperature dependence of the dissociation rates must be modelled correctly, which also requires BIRD experiments over a wide temperature range.

Master equation modelling is particularly difficult for water clusters, as the water molecule is mobile, and often several low-lying isomers are populated. Recently, we developed a new multiple well approach for master equation modelling, where multiple isomers are taken into account. We showed for hydrated carbonate clusters [1], that this multiple well approach can improve the accuracy of the energetics. Now, the new approach is tested on hydrated $CO_4^{\bullet-}$. Experimentally, we observe for $CO_4^{\bullet-}(H_2O)$ loss of water and for $CO_4^{\bullet-}(H_2O)_2$ loss of water as well as loss of CO_2. This additional channel and the growing number of local minima increase the complexity of the master equation model. Different further improvements for the master equation model are tested, including the description of a roaming water molecule as a particle in a box and the consideration of tight transition states that connect selected isomers.
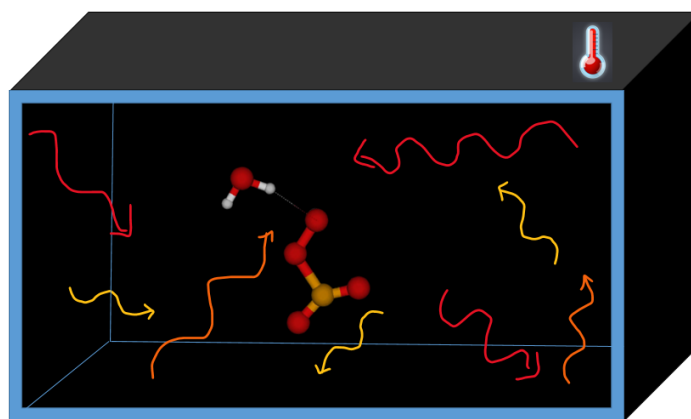

Figure 1: Blackbody infrared radiative dissociation of hydrated peroxycarbonate radical anions

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Observation of Penning Electron Detachment by Electronically-Excited Potassium Atoms in High Rydberg States

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Penning ionization is a well-studied process where neutral atoms or molecules are ionized by collisions with partners in electronic excited states $(A + N^* \rightarrow A^+ + N + e^-)$. In analogy with this, Penning detachment is a process where electronically excited energy donors collide with anions to free the excess electron $(A^- + N^* \rightarrow A + N + e^-)$. The cross sections of Penning detachment have been investigated both theoretically [1-3] and experimentally [4-6] to achieve better understanding of the kinetic processes in the stellar atmosphere and D-region of ionosphere. While the Penning detachment cross section is predicted to be heavily dependent on the excited states of the neutral collision partners, their relation is not fully investigated experimentally.

In this study, Penning detachment of SF_5^- by excited potassium was observed, and its dependence on the excitation energy of potassium was investigated. SF_5^- anion was generated by introducing sulfur hexafluoride into the laser photoemission ion source. SF_5^- ion beam was crossed with potassium atoms in Rydberg excited states. Figure 1 shows the mass spectra of SF_5^- with the presence of potassium in ground state (Fig1 (a)) and 24d Rydberg excited state (Fig1 (b)), which show significant depletion of SF_5^- ion signal by excited potassium. By scanning the Rydberg states of potassium from 9d to 30d, the dependence of depletion efficiency on the excitation energy was observed.
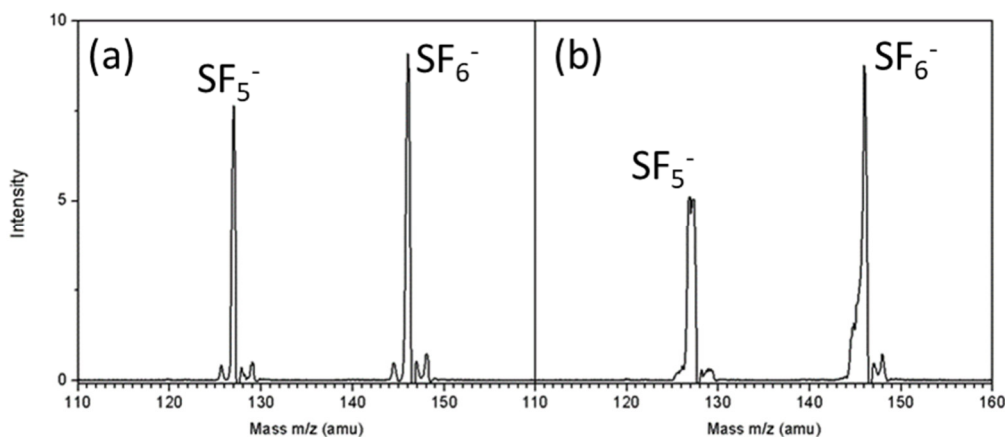

Figure 1: Mass spectra of SF_5^- (a) crossed with ground state potassium (b) crossed with excited potassium in 24d Rydberg state.

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Small Silicon Oxide Clusters – Optical Photodissociation and Photochemical Properties

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An essential constituent in the evolution of solar systems, planets – like the Earth – and other celestial bodies is interstellar dust, whose key components are µm-sized silica and metal silicates [1]. Currently, among the possible precursors for macroscopic dust grains, only molecular SiO has been identified in interstellar regions and circumstellar disks [2]. Experimental measurements on polyatomic $Si_nO_m^+$

Figure 1: Summed mass spectra of genera small $Si_nO_m^+$ clusters and schematic of the used la vaporization setup.

cations, in combination with quantum chemical calculations, are expected to answer open questions on further intermediates of the dust grain formation. Consequently, we present the first optical spectra for $Si_nO_m^+$ cations larger than SiO^+ and Si_2^+ [2, 3]. Photodissociation spectroscopy of mass-selected ions in a tandem mass spectrometer coupled to a laser vaporization source (Figure 1) is used to determine electronic and optical properties of the clusters under investigation [4]. Electronic photodissociation data generated by action spectroscopy are compared and interpreted with TD-DFT calculations (Figure 2).
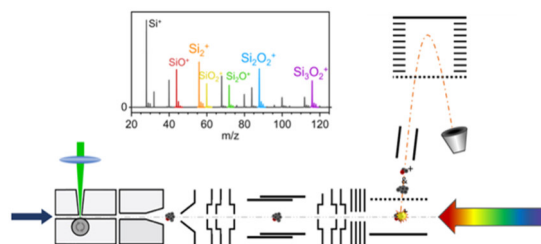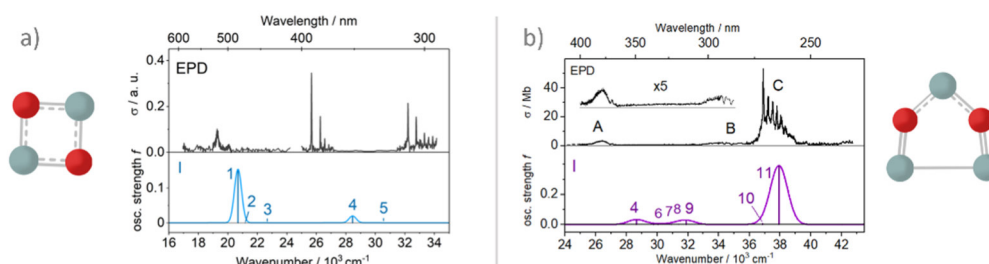

Figure 2: Calculated ground state structures of the lowest lying isomers fou measured EPD spectra and comparison to vertical TD-DFT spectra of a) $Si_2O_2^+$ (UB3L D3/aug-cc-pVQZ) and b) $Si_3O_2^+$ (UCAM-B3LYP-D3/cc-pVTZ)

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A modified particle in a box model

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Adamantane and diamantane are molecules with a cuboid carbon structure and are discussed to be possible carriers for diffuse interstellar bands. In recent work, the optical spectra of the adamantane and diamantane radical cations (Ada^+, Dia^+) were measured for the first time [1, 2]. Ada^+ and Dia^+ both have similar electronic $D_2(^2E_{(u)}) \leftarrow D_0(^2A_{1(g)})$ transitions at 1.853 and 1.710 eV, respectively. In this work, we try to explain the energetic red shift between both transitions with a sophisticated particle-in-a-box model.

It turns out that one does not get reliable results using the classical particle-in-a-box model. Therein, we modify this simple model by adding an interior infinite potential into a small region in the box. The stationary Schrödinger equation for the modified model is solved analytically with the help of the Python library SymPy [3]. With the modified model, we are able to calculate the red shift of the electronic transitions from Ada^+ to Dia^+. Furthermore, it is possible to estimate the carbon valence electron radius. We discuss the effect of electron-donating and electron-withdrawing substituents. Lastly, we apply the model to similar cuboid molecules like cubane.

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Ionization and Dissociation Energies of Dysprosium Monoxide, DyO

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Understanding of lanthanide oxides (LnO) is challenging due to their complex electronic structure, which results from the open 4f (except Lu) and 5d valence shells of the Ln atoms. A motivation for the study of such molecules is the chemi-ionization reaction: $Ln + O \rightarrow LnO^+ + e^-$ [1]. This associative ionization reaction requires that the ionization energy (IE) of the molecule is lower than its Ln-O binding energy (D0) and thus exothermic ($\Delta H_0 = IE - D_0 < 0$). Notably, such formation reaction can proceed also in extremely dilute environments, like the interstellar medium, as stabilization of the dimer is reached without the need of third body collisions or radiative cooling. This is comparably unusual for small diatomic molecules. So far, associative ionization has already been observed in the oxidation of a number of transition and lanthanide metals, including praseodymium, neodymium, samarium, and gadolinium.

Previous reports for the oxidation of dysprosium atoms are contradictory. Thermochemical studies and electron impact ionization led to estimates for IE and D_0 of DyO, but the values are associated with large uncertainties. Furthermore, a recent measurement of $D_0(DyO^+)$ implies $\Delta H_0 = +0.33(2)$ eV, however, this conflicts with the earlier reported values for IE and D_0 [2].

Here we report on the characterization DyO and DyO^+ in a supersonic molecular beam by applying a variety of spectroscopic approaches using different REMPI and PFI schemes, MATI, and (V)UV single-photon ionization. Isotope specific excitation schemes allow to obtain rotationally resolved spectra, and several Rydberg-series converging to the ionization limits of different rotational states of DyO^+. The Rydberg series can be clearly assigned starting with the lowest J=7.5 state. Beside these long-living Rydberg molecules, a number of short-lived molecular states are found. From the spectroscopic data obtained for the fermionic [161]DyO and the bosonic [162]DyO, the values of IE and D_0 are determined with a high precision. This leads to the conclusion that the reaction $Dy + O \rightarrow DyO^+ + e^-$ clearly proceeds exothermic.

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Gas-Phase CuPd Bimetallic Cluster-Modified Electrodes as Model Electrocatalysts for CO$_2$ Conversion

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Copper-based electrocatalysts possess the unique ability to convert CO$_2$ to multicarbon products such as ethylene – a precursor in many industrial processes. However, their stability and product selectivity remain insufficient. A promising approach to overcome these shortcomings and design better CO$_2$RR electrocatalysts is to tune Cu selectivity by forming bimetallic Cu-M systems [1] while establishing their detailed structure-selectivity relationship. To achieve this, we used laser ablation Cluster Beam Deposition (CBD) [2] to produce well-defined bimetallic cluster-modified electrodes [2]. More specifically, CuPd clusters with an original average size of 2.5 nm and mass loadings of 1-2 µg cm^{-2} were deposited onto a carbon support. To produce a model catalyst which allows the independent investigation of the electronic and geometric structural effects induced to Cu by the second element, a Cu$_{0.9}$Pd$_{0.1}$ composition was selected [3]. CuPd cluster-decorated electrodes were tested for CO$_2$ electrolysis and methane (C$_1$), and ethylene (C$_2$) were found among the products. As it is shown from the electrocatalytic activity trends, the evolution of C$_2$ products is correlated with the cluster mass loading. In addition, the cluster coverage influences the onset of the competitive H$_2$ production (HER). High resolution (Scanning) Transmission Electron Microscopy ((S)TEM) coupled with Energy-dispersive X-ray spectroscopy (EDX), and X-ray Photoelectron Spectroscopy (XPS) analyses of the as-prepared cluster-modified electrodes, show that the clusters feature some degree of CuPd alloying in the ambient. CuPd cluster-based systems will then be investigated in-situ using X-ray absorption spectroscopy to unravel their structure-catalytic performance relationship.

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In situ (S)TEM Characterization of a Pd/ZnO Catalyst for CO$_2$ Hydrogenation and Selective Methanol Synthesis

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Pd/ZnO has been recognized as an effective catalyst for the conversion of CO$_2$ into methanol. While the Pd-Zn alloy phase has traditionally been seen as the key active component, methanol formation does not occur in the presence of an inert oxide support (such as Al$_2$O$_3$ or SiO$_2$), indicating that the presence of both zinc oxide and palladium or palladium-zinc phases is necessary to achieve high activity and selectivity for methanol under industrial conditions.

To optimize the Pd/ZnO catalytic performance we need a thorough understanding of the reaction mechanism and active site structure, as well as the nature of active sites during reaction conditions. *In-situ* Scanning Transmission Electron Microscopy (S)TEM can provide a deeper understanding of the changes occurring at the nanometer and atomic scale when catalytic clusters are exposed to aggressive reaction environments, which in turn have a major impact on their catalytic behavior[1]. In our study, Pd clusters are prepared using a magnetron sputtering cluster source and are deposited on ZnO powders. The catalyst was drop-casted on the bottom chip of a MEMS nanoreactor to monitor the reduction process.

In situ reduction in the TEM was carried out at 350 ˚C, using a reactant gas mixture of 5:95 ratio of H$_2$:He with a flow of 0.1 ml/min, and by maintaining the pressure at 500 mbar for 1 hour. High resolution (S)TEM imaging allowed us to track the structural changes of the Pd clusters on the ZnO support. The measured interatomic distances agree with the PdZn alloy tetragonal structure, confirming the formation of an alloy during the reduction step.

Currently, the deposition of clusters on powders is limited to very low loadings. In our lab, we recently designed a chip holder to mount the *in situ* bottom chip inside the cluster source, an approach that can allow for higher cluster loadings to be achieved. The chip windows will accommodate the drop-casted support material and the clusters will be deposited directly on the support's surface. Moreover, the holder can house a shadow mask for a more critical deposition to certain regions of interest. With this improvement, we can study more particles and perform complementary (S)TEM spectroscopic techniques. This will not only allow for better statistics on more particles, but also clarify the role of the palladium-zinc alloy phase in facilitating this reaction.

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Stable mass-selected AuTi nanoparticles for CO oxidation

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Addressing stability in reactive conditions is a big challenge when working with clusters and nanoparticles[1]. The stability of < 5 nm gold nanoparticles has been a central focus since their catalytic properties were discovered. To enhance their stability during CO oxidation at high temperatures, one common approach involves modifying their interactions with the supporting material, while another approach involves incorporating another metal into the nanoparticles themselves, forming an alloy with gold. Previous studies have suggested that AuTi alloy nanoparticles could offer improved stability[2,3]. This research presents direct observations that demonstrate the enhanced stability of AuTi alloy nanoparticles compared to pure Au nanoparticles during CO oxidation. The alloyed nanoparticles exhibited activity comparable to that of the pure Au nanoparticles, but they displayed significantly higher stability at elevated temperatures. Detailed investigations employing Low Energy Ion Scattering, X-ray Photon Spectroscopy, and Environmental Transmission Electron Microscopy unveiled the structure of the AuTi nanoparticles. These characterizations revealed an Au core surrounded by an alloy shell consisting of AuTi. Remarkably, this structure remained stable even under reactive conditions at 320°C, and an incremental increase in activity was observed over a duration of more than 140 hours. This work reaffirms the potential of nanoparticle alloying as a mean to tune both catalytic activity and stability, emphasizing the importance of employing complementary and in-situ characterization techniques to advance the optimization of nanoparticle catalyst design.
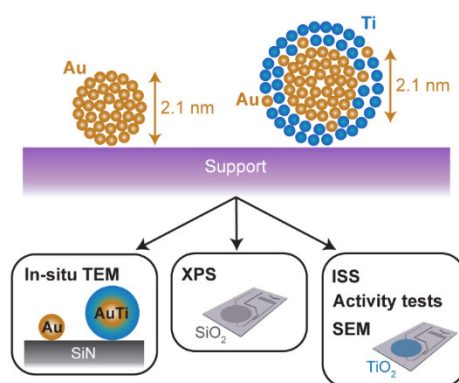

Figure 3: Overview of methods and substrates for catalyst characterization[4].

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Size-studies of Au and Cu nanoparticles for CO_2 electroreduction: every parameter counts

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Nanoparticles are extensively utilized in various industrial processes due to their enhanced catalytic performance resulting from a high surface-to-bulk ratio. Modulating the size of these nanoparticles allows for manipulation of their activity and selectivity[1,2], which is particularly intriguing in the context of CO_2 electroreduction, a process yielding 16 different products where enhancing selectivity is of significant interest[3]. However, investigating these minute catalysts in electrochemistry poses considerable challenges, given the multitude of parameters that influence apparent selectivity.

In this study, we thoroughly examine the intrinsic selectivity of size-selected nanoparticles by meticulously controlling all relevant parameters, including size, loading, impurities, and shape. Our methodology aims to meticulously manage these variables to establish experimental structure-activity relationships and generate reliable, transferable knowledge applicable to other catalytic studies, both fundamental and experimental. Here, we present several parameters with significant impacts on the selectivity and activity of the nanocatalysts, along with the results demonstrating the influence of these controlled parameters on the accuracy of size-based performance studies of the nanoparticles.
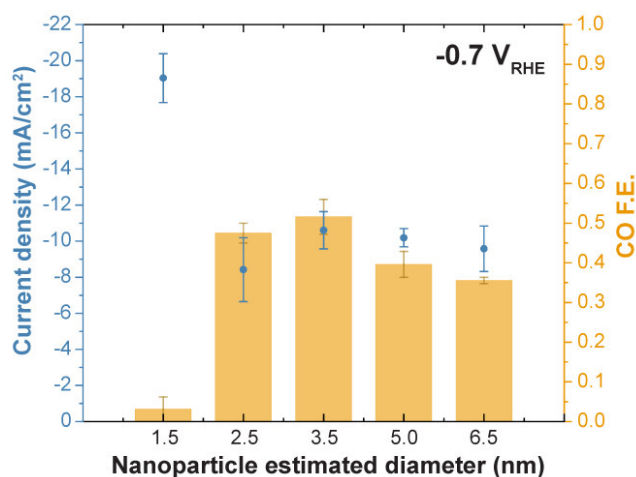

Figure 4. Size study on the CO faradaic efficiency of Au nanoparticles

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Size dependence of catalytic activity of well-defined Pt nanosystem supported on CeO₂ for CO oxidation reaction

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Supported metal catalysts are complex systems whose performance depends on various materials parameters and synergistic effects. Through the use of ligands, advanced techniques in cluster / small nanoparticle (NP) synthesis allow precise control over the particle size and even the number of active metal atoms in clusters, and thus the development of well-defined powder model catalysts [1,2]. Polyol reduction is a flexible method that enables the synthesis of both well-defined NPs and atomically precise clusters starting from various precursor compounds dissolved in high-boiling polyols [3].
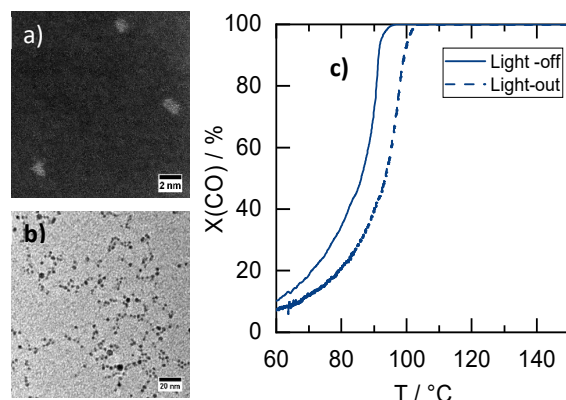

Figure 1. a) STEM-HAADF image of $Pt_{17}(PPh_3)_8(CO)_{12}^{2+}$ cluster [4]; b) TEM image of Pt NPs with average size of 3.5nm; c)Light-off/Light-out curves for CO oxidation catalysis of Pt NPs anchored on CeO₂

We show the synthesis of platinum clusters and NPs within a size range from 1 to 5 nm *via* a polyol process using different types of ligands and reaction conditions. The clusters and NPs were analyzed by electron microscopy with energy-dispersive X-ray analysis (TEM, STEM-HAADF, EDS), infrared spectroscopy (FT-IR, ATR), dynamic light scattering (DLS), mass spectroscopy (MS) and optical emission spectroscopy with inductively coupled plasma (ICP-OES). We anchor the clusters and NPs on a metal oxide support to prepare model catalysts for emission control catalysis. The influence of cluster / NP size on the catalytic performance was investigated for CO oxidation.

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Structure-selectivity of $Cu_{2-x}Se$ towards CO_2 electroreduction

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Copper selenides, forming both non-stoichiometric and stoichiometric phases, are an important family of transition metal chalcogenides (TMCs) [1]. Despite their promising electrocatalytic performance, active site identification in $Cu_{2-x}Se$ nanostructures remains a challenge. The varying product selectivity among similar nanostructures, yielding products like formic acid [2], CO [3], and methanol [4], highlights the need to understand structure-performance relationships for improved $Cu_{2-x}Se$ electrocatalyst design. This work highlights the structure-selectivity relationship in $Cu_{2-x}Se$ under CO_2 electroreduction at -1.4 V_{RHE} yielding 23% of methanol in its pristine form and 82.1% CO at partial current density of 27.7 mA cm^{-2} after chemical- (H_2O_2 etching) and electro-activation. Low and high magnification STEM images reveal that the pristine $Cu_{2-x}Se$ catalyst is comprised of $Cu_{1.71}Se$ wires with a cubic structure while the chemically activated one $[Cu_{2-x}Se]O_y$ displays wire-like characteristics enveloped by thin, folded oxide layers. In situ Raman under electro activation of $[Cu_{2-x}Se]O_y$ at -1.6 V shows a drastic reduction of the Cu-Se bond signal with time suggesting a degradation of the CuSe while a Cu_2O signal appearing and constantly growing once the potential is returned to OCP suggests that metallic Cu segregated under electro-activation is then oxidized into Cu^{1+} after activation. Ex situ EXAFS of $[Cu_{2-x}Se]O_y$ confirms the progressive transformation of the $Cu_{2-x}Se$ into $Cu_{1-z}Se$ phase through segregation of Cu that forms a mixture of Cu^{1+} and Cu^{2+} after reaction. A more moderate Cu segregation also occurs in pristine $Cu_{2-x}Se$ as no $Cu_{1-z}Se$ phase transformation is detected. In good agreement with EXAFS, post-activated catalysts reveal the presence of agglomerates of Cu_2O cubes (cubic, Pn-3m) with 50 to 90 nm edges amidst smaller $Cu_{2-x}Se$ particulates. The copper selenide system's changing selectivity, which depends on activation, could be explained by the combined impact of copper segregation and the interactive effects between metallic Cu and the residual structures of $Cu_{2-x}Se$ or $Cu_{1-z}Se$.
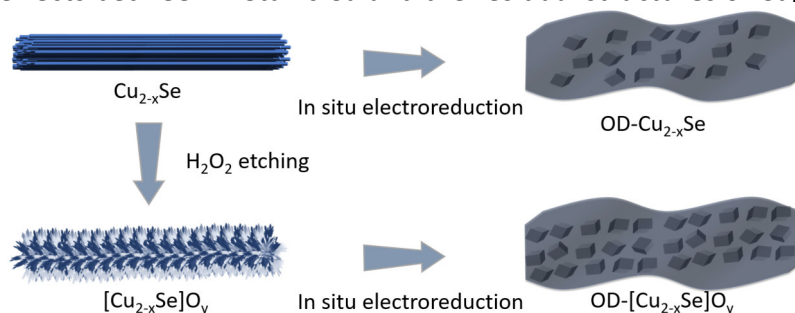

Figure 1: In situ structural evolution of $Cu_{2-x}Se$-coated Cu_2O nanocubes

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